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Efficient hydrogenation of furfural to fufuryl alcohol over hierarchical MOF immobilized metal catalysts

Ruiqi Fang, Liyu Chen, Zirong Shen, Yingwei Li*

State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO	ABSTRACT		
Keywords: Biomass Furfural Hydrogenation Heterogeneous catalysis Metal-organic frameworks	Transformation of furfural, a typical biomass-derived robust platform molecule, into value-added chemical furfuryl alcohol has drawn intense attention. The conventional supported catalysts which are restricted in the		
	microporous regime suffered from high mass diffusion resistances and limited catalytic activity. We herein demonstrate the synthesis of a series of transition-metal catalysts by using hierarchical porous H-UiO-66 as the support for highly efficient conversion of furfural to furfuryl alcohol. The unique nanoarchitecture endows the catalyst with low mass diffusion resistance, high accessibility of metal active sites and high durability in the liquid phase reaction. A nearly quantitate yield of furfuryl alcohol was achieved over the Pd/H-UiO-66 catalyst at 60 °C. 0.5 MPa H ₂ in the acueous medium within 3 h		

1. Introduction

Exploring biomass resources provides an efficient solution to the fossil energy diminishing and the resultant environmental problems such as acidic rains, greenhouse effect and atmosphere pollutions [1–3]. Lignocellulose is the most abundant biomass compound all over the world, which is not only renewable but also carbon neutral and has shown great potential in replacing fossil resources to produce fuels and chemicals [4–6]. However, the large molecular weight and complex compositions of raw lignocellulosic feedstocks limit their direct utilization [7–9]. In this concern, their small molecular derivatives including sugars and furans, which are regarded as the key platform molecules linking raw biomass and value-added products, have attracted much research interest [10,11].

Furfural (FFA) is a typical representative of the furanic platform molecules derived from acidic hydrolysis of pentose (and hemicellulose) and could be transformed into various value-added bio-chemicals including furfuryl alcohol (FOL) and cyclopentanone [12]. FOL is one of the most important derivatives of FFA, whose production consumes over 65 % of the overall FFA synthesized. FOL is mostly utilized as high-quality cores and moulds in the foundry industry, and is also an essential solvent in the preparation of polyurethane foams in the refractory industry. Moreover, FOL is a versatile intermediate in the synthesis of fragrances and pharmaceuticals [13–15]. Currently, FOL could be produced through gas and liquid phase hydrogenation of FFA, and the latter one is much preferred due to its higher catalytic efficiency to obtain FOL in desirable yields [16]. In early years, homogeneous catalysts (e.g., copper chromite, Ru(II) complexes, etc.) were employed in the FOL synthesis at high temperatures and H_2 pressures (e.g., 140 °C, and 10 MPa). Despite of the excellent FOL yields (> 90 %), severe pollutions and toxicity are not suitable to meet the strict environmental regulations [17,18]. Nowadays, modern chemical industry calls for highly efficient catalytic systems under green and mild reaction conditions. Thus, much effort has been devoted to exploring highly active and selective catalytic systems and green reaction routs of FFA into FOL.

In the past few years, numbers of metal catalysts based on different supports (e.g., metal-organic frameworks (MOFs), active carbons, silicates and metal oxides) were designed and fabricated for furfural transformation [19–21]. As an example, Guan's group reported a highly active Ru/Zr-MOFs catalyst for FFA hydrogenation, achieving a 95 % FOL yield under mild conditions (20 °C, 0.5 MPa H₂) with a TOF value of 11 h^{-1} [22]. Liu et al. prepared a Ir-ReO_x/SiO₂ catalyst, affording a complete conversion of FFA and 97 % yield of FOL at 50 °C and 6 MPa H₂ [23]. Fulajtárova et al. synthesized a PdCu/MgO catalyst for FFA hydrogenation, 99 % yield of FOL was obtained under the optimized reaction conditions [24]. In spite of the excellent FOL yields achieved, most of the reported catalysts are restricted to the microporous regime (pore size < 2 nm), stable but suffer from high mass diffusion resistances, which to some extent would restrict the further enhancement of reactivity. Oppositely, mesoporous catalysts (2-50 nm) may facilitate the mass diffusion and enhance the accessibility of the active sites

* Corresponding author.

E-mail address: liyw@scut.edu.cn (Y. Li).

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on the internal surface, but would collapse during the reaction processes, far from meeting the regulations of long-term applications. In these regards, hierarchical porous materials (such as hierarchical MOFs, denoted as H-MOFs), taking both advantages of microporous and mesoporous materials, are believed to be promising candidates [25–30]. However, seldom attention has been paid on the synthesis of highly active and durable MOFs-based catalysts for liquid-phase biomass-related conversions.

Herein, we demonstrate the synthesis of a series of transition-metal catalysts supported on a hierarchical porous MOF (i.e., H-UiO-66) for highly efficient transformation of FFA to FOL. Benefitting from the uniformly distributed Pd nanoparticles (NPs) and unique hierarchical porosity of the H-UiO-66 support, the as-prepared Pd/H-UiO-66 catalysts achieved a complete conversion of FFA with > 99 % FOL selectivity under 60 °C and 0.5 MPa H₂. The TOF value was as high as $66.7 h^{-1}$, outperforming the previously reported supported metal catalysts. More importantly, the integrality of the catalyst retained well even after up to ten runs, and no obvious activity loss was observed. Additionally, the effects of various reaction parameters (including metal loadings, reaction temperatures, H₂ pressures and solvents) on the catalytic performances were also investigated.

2. Experimental

2.1. Materials

All reagents were of analytical grade and were used without further purification.

2.1.1. Synthesize of UiO-66

UiO-66 was synthesized through a solvothermal strategy. In a typical synthesis, $ZrCl_4$ (133.6 mg), terephthalic acid (100.0 mg), concentrated hydrochloric acid (360 µL) and N,N-dimethylformamide (DMF) (40 mL) were sealed and heated at 120 °C for 24 h. The resultant powder was obtained after washing with DMF and drying under vacuum at 50 °C overnight.

2.1.2. Synthesis of H-UiO-66

The H-UiO-66 was synthesized following the above procedures with some modifications. Typically, $ZrCl_4$ (133.6 mg), terephthalic acid (50.0 mg), benzoic acid (36.8 mg), N,N-dimethylformamide (DMF) (40 mL) and concentrated hydrochloric acid (360 µL) were sealed and heated at 120 °C for 20 h. The resultant powder was obtained after washing with DMF and drying under vacuum at 50 °C overnight.

2.1.3. Synthesis of supported M/UiO-66 and M/H-UiO-66 (M = Pd, Pt, Au and Cu)

The catalysts were synthesized through the same impregnation method: a certain amount of MCl_x salts and MOFs (UiO-66 and H-UiO-66) (300 mg) were dissolved in 3 mL H₂O and stirred for 24 h at room temperature. Then, the resulting powder was isolated and heated at 250 °C for 2 h under H₂ flow (N₂ was utilized in advance to remove the residual air). The as-prepared materials were denoted as M/UiO-66 and M/H-UiO-66 (M = Pd, Pt, Au and Cu).

2.2. Catalyst characterization

Powder X-ray diffraction (PXRD) patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Ka radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm). BET surface areas and pore size measurements were performed with N₂ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 M instrument. Before measurements, samples were degassed at 100 °C for 12 h. The metal dispersion was characterized by H₂ chemisorption experiments. Two isotherms were measured at 77 K with the intermediary evacuation treatment, the difference of which gave the irreversible chemisorption

of H₂. The Pd contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument. The size and morphology of materials were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was carried out on a Zeiss Merlin instrument. TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were recorded on a JEOL JEM-2010 F instrument equipped with EDX analysis (Bruker XFlash 5030 T) operated at 200 kV. XPS measurements were performed in a ultra-high vacuum (UHV) multipurpose surface analysis system (SpecsTM model Germany) operating at pressures $< 10^{-10}$ mbar using a conventional X-ray source (XR-50, Specs, Mg Kalpha, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. Deconvolution curves for the XPS spectra were obtained using software supplied by the spectrometer manufacturer. ATR-IR measurements were carried out on a Thermo FisheriS10 equipped with a liquid nitrogen cooled MCT detector. The spectra were obtained by averaging 32 scans at the resolution of 1 cm^{-1} . The thin film of the catalyst powder deposited on the ZnSe element for the ATR-IR spectroscopic study was prepared as follows. A suspension of ca. 132 mg of the catalyst powder and 5 mmol of FFA in 5 mL H₂O was stirred overnight to eliminate any agglomeration, after which, the slurry was dropped onto the ZnSe internal reflection element (IRE) for recording the spectra. The IR spectrum of the pure catalyst in the solvent was acquired as the background.

2.3. General procedures for FFA hydrogenation

In a typical run, FFA (5.0 mmol) and catalyst (metal 0.3 mol%) were added to H_2O (5.0 mL) in an autoclave equipped with magnetic stirrer. After purging the reactor several times with H_2 , the reactor was heated to 60 °C and subsequently purged with 0.5 MPa H_2 with a stirring speed of 600 rpm. During the reaction, samples were taken and analyzed by GCMS (7890 GC/5975C MS) equipped with a HP-innowax capillary column (30 m × 0.25 mm). The first sample was taken when the H_2 pressure was purged to 0.5 MPa. After reaction, the reactor was cooled to room temperature and the catalyst was isolated from the solution by centrifugation, washed with methanol and reused directly. The conversion and selectivity were evaluated on the basis of the amounts of furfural. The conversion of furfural (mol%), products yield (mol%) and furfuryl alcohol selectivity (mol%) were calculated using the following equations:

Furfural conversion = (1- $n_{furfural}/n_{furfural loaded})$ × 100 %

$$\begin{aligned} \text{Product selectivity} &= \frac{\text{Moles of product}}{\text{Moles of furfural converted}} \, n_{\text{product}} / n_{\text{furfural converted}} \\ &\times 100\% \end{aligned}$$

$$\begin{aligned} \text{Furfuryl alcohol yield} &= \frac{\text{Moles of cyclopentanone}}{\text{Moles of furfural loaded}} n_{\text{furfuryl alcohol}} / n_{\text{furfural loaded}} \\ &\times 100\% \end{aligned}$$

3. Results and discussion

3.1. Synthesis and characterization of M/H-UiO-66

The highly stable UiO-66 and its hierarchically porous derivative H-UiO-66 employed in this work were synthesized through a solvothermal strategy [31]. The supported M/UiO-66 and M/H-UiO-66 (M = Pd, Pt, Au, Cu) catalysts were prepared by using an impregnation method, during which the M ions were firstly adsorbed within MOF crystals and subsequently reduced to form NPs. The powder X-ray diffraction (XRD) patterns of the as-prepared materials matched well with that of the parent MOF, indicating the crystal structure was well preserved after



Fig. 1. XRD patterns of the as-prepared materials.

 Table 1

 Characterization results of the as-prepared materials.

Samples	Metal contents (wt%)	$S_{BET} (m^2 g^{-1})$	V_{pore} (cm ³ g ⁻¹)
UiO-66	-	1035	0.41
H-UiO-66	-	462	0.56
Pd/UiO-66	2.00	961	0.38
Pd/H-UiO-66	2.00	416	0.54
Au/H-UiO-66	1.93	398	0.53
Pt/H-UiO-66	1.96	410	0.54
Cu/H-UiO-66	1.98	404	0.53
Pd/H-UiO-66 reused	2.00	396	0.49

metal doping (Fig. 1). Diffraction peaks of the transition metals (Pd, Pt, Au and Cu) could not be observed, which could be resulted from their low contents $(1.9 \sim 2.0 \text{ wt\%}, \text{Table 1})$ and small particle sizes.

The porosity properties of the as-prepared materials were evaluated by N_2 sorption experiments. The type I isotherm and pore size distribution of the pristine UiO-66 indicated its typical microporous nanostructure [31]. As expected, the H-UiO-66 exhibited a type IV isotherm, showing a significant loss of N_2 uptake and obvious hysteresis loop at low (< 0.1) and medium (> 0.45) P/P₀ ranges, respectively,

which were attributed to the partial loss of micropores and formation of mesopores due to the introducing of the benzoic acid ligands (Fig. 2a). Accordingly, in comparison with the pristine UiO-66, the Brunauer-Emmett-Teller (BET) surface area of H-UiO-66 was significantly decreased to $462 \, \text{m}^2 \, \text{g}^{-1}$ and the pore volume was enhanced to $0.56 \text{ cm}^3 \text{g}^{-1}$ with a wide pore size distribution (Fig. 2b and Table 1). For the supported Pd/UiO-66 and M/H-UiO-66 (M = Pd, Pt, Au, Cu) materials, slight decrements in BET surface areas and pore volumes could be observed, suggesting the metal NPs may block some of the pores of the supports (Table 1). In the X-ray photoelectron spectroscopy (XPS) spectra, the binding energy of Pd $3d_{5/2}$, Pt $4f_{7/2}$, Au $4f_{7/2}$ and Cu 2p_{3/2} peaks at *ca.* 335.5 eV. 71.2 eV. 84.2 eV and 933.2 eV could be assigned to the metallic state of Pd. Pt. Au and Cu species in the M/H-UiO-66 materials, respectively (Fig. 3 and Fig. S1-S4) [32-35], indicating the transition metal NPs were reduced after the calcination process in H₂ flow.

Scanning electron microscopy (SEM) images of the parent UiO-66 pointed out its octahedral morphology in the size of ca. 1 µm with smooth surfaces (Fig. 4a and b). On the contrary, with the introduction of defective ligands benzonic acid, the as-prepared H-UiO-66 supports exhibited the hierarchically porous structure with uniformly distributed pores on the rough external surfaces (Fig. 4c and d). The Pd NPs could not be clearly observed in SEM images because of their small particle sizes. Transmission electron microscopy (TEM) images of a single H-UiO-66 crystal exhibited its much spongy and transparent nanoarchitecture in comparison with the pristine UiO-66, which was related to the formation of hierarchical pores throughout the MOF bulks (Fig. 4eg). Additionally, the homogeneous distribution of Pd NPs could be found on the H-UiO-66 supports as black dots with the average sizes of ca. 3 nm without any significant aggregations (Fig. 4h), in agreement with the XRD results. Additionally, the high-angle annular dark-field scanning TEM (HAADF-STEM) images and elemental mappings verified the homogeneous distribution of Pd NPs on the H-UiO-66 supports.

3.2. Catalytic activity of M/H-UiO-66 in FFA hydrogenation

The obtained materials were subsequently employed as catalysts in the selective hydrogenation of FFA to FOL. The reactions were carried out at 60 °C, 0.5 MPa H₂ using H₂O as the solvent. After reaction, products were isolated and subsequently analyzed by gas chromatography–mass spectrometry (GC–MS). For comparison, control experiments using the pristine UiO-66 and H-UiO-66 as catalysts showed no FFA conversion, suggesting the critical role of metal sites for the hydrogenation process. To our delight, the M/H-UiO-66 (M = Pd, Pt, Au, Cu) catalysts exhibited moderate to excellent catalytic efficiency,



Fig. 2. N_2 adsorption isotherms (a) and pore-size distributions (b) of the as-prepared materials.



Fig. 3. XPS spectra of Pd 3d of Pd/H-UiO-66 (a), Pt 4f of Pt/H-UiO-66 (b), Au 4f of Au/H-UiO-66 (c) and Cu 2p of Cu/H-UiO-66 (d).

achieving 47~100 % FFA conversions and 11~99 % FOL yields at a relatively low metal loadings (0.5 mol%). Typically, the Pd/H-UiO-66 catalyst outperformed the others with a complete FFA conversion and > 99 % FOL yield. The calculated TOF value was as high as 66.7 h⁻¹, which was significantly enhanced by the factor of *ca.* 1.2~2.1 in comparison with the other catalysts under the investigated reaction conditions (Table 2).

The Pd dispersions of the Pd/UiO-66 and Pd/H-UiO-66 catalysts were characterized through hydrogen chemisorption conducted under 77 K. Two isotherms were obtained over each catalyst, representing the total amount of chemisorbed hydrogen and reversible chemisorbed hydrogen, respectively (Fig. S5). Besides, the difference between these isotherms indicated the irreversible fraction of hydrogen on the metallic Pd [37]. As the uniform sizes and homogeneous dispersion of the Pd NPs, the dispersions of Pd in Pd/H-UiO-66 and Pd/UiO-66 were calculated to be ca. 0.42 and 0.31, respectively. The higher Pd dispersion pointed out a significantly enhanced accessibility of Pd active sites of the Pd/H-UiO-66, leading to higher hydrogenation reactivity as compared with Pd/UiO-66.

In situ ATR-IR experiments were conducted to further elucidate the high reactivity of Pd/H-UiO-66 in FFA hydrogenation. As exhibited in Fig. 5, the FFA characteristic bands could be clearly observed at 1670 cm^{-1} and 1540 cm^{-1} , which were assigned to C=O and C=C stretching bonds, respectively [36]. Noteworthy, the intensity of these bands over the Pd/H-UiO-66 was significantly higher, implying a stronger adsorption of FFA and enhanced accessibility of Pd active sites on the Pd/H-UiO-66 catalyst. Consequently, the rich mesopores of the

H-UiO-66 support would enhance the accessibility of the Pd active sites and facilitate the diffusion and adsorption of FFA molecules, thus played a key role in promoting the catalytic efficiency over Pd/H-UiO-66.

We further studied the effect of Pd loadings on the catalytic performance. A series of Pd/H-UiO-66 with 0.5–3.0 wt% Pd loadings were synthesized and employed in FFA hydrogenation, and the reaction results are exhibited in Fig. 6a. When increasing the Pd loadings from 0.5 to 2.0 wt%, the catalytic activity gradually increased, and a nearly quantitative yield of FOL was obtained over the 2.0 wt% Pd/H-UiO-66 catalyst within 3 hours. With a further increment of metal content to 3.0 wt%, a significant decrement of catalytic activity was observed, which could be attributed to possible aggregation of Pd NPs at the high loading.

We also investigated the effects of reaction temperatures, H₂ pressures and solvents on the catalytic performances of the Pd/H-UiO-66. With an increase in the reaction temperatures from 40 to 60 °C, a significant improvement of FFA conversion was observed from 73 to 100 %, maintaining the > 99 % selectivity to FOL (Fig. 6b). Besides, higher temperatures (> 60 °C) led to higher catalytic activity but the generation of unwilled byproducts (*e.g.*, 2-methylfuran). The same tendency could also be observed in the pressure examination, and 0.5 MPa H₂ pressure was optimum to obtain the high FFA conversion and FOL selectivity simultaneously (Fig. 6c). Besides, in comparison with toluene, dimethyl sulfoxide (DMSO) and ethanol, H₂O was believed to be the best solvent in terms of both FFA conversion and high FOL selectivity (Fig. 6d).

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Fig. 4. SEM (a, b, c and d) and TEM (e, f, g and h) images of the UiO-66 (a, b, e and f) and Pd/H-UiO-66 (c, d, g and h), and STEM image and corresponding elemental mappings of Pd/H-UiO-66 (i).

Table 2

Reaction results of FFA hydrogenation over different catalysts.^a

$ \begin{array}{c} & & \\ & & $								
Catalysts	Metal loadings (mol%)	Conversion (%)	FOL Selectivity (%)	FOL yield (%)	TOF (h ⁻¹)			
UiO-66 H-UiO-66 Pd/UiO-66 Pd/H-UiO-66 Au/H-UiO-66 Pt/H-UiO-66 Pd/H-UiO-66 Pd/H-UiO-66	- 0.50 0.50 0.50 0.50 0.50 0.50	- 63 100 85 78 47 100	- > 99 > 99 88 63 23 97	- 62 > 99 75 49 11 97	- 42.0 66.7 56.7 52.0 31.3 66.7			

^a Reaction conditions: FFA 5.0 mmol, 0.5 MPa H₂, 60 °C, H₂O 5 mL, 3 h.

The durability of the catalysts, which is crucial for long-term utilization in liquid-phase reactions, was also tested. After reaction, the Pd/ H-UiO-66 catalyst was isolated and directly reused after washing. No significant activity or selectivity loss of Pd/H-UiO-66 could be observed even after 10 cycles, and the TOF values remained almost unchanged $(66 \sim 66.7 h^{-1})$ (Fig. 7a). The XRD diffraction patterns and N₂ sorption results of the reused Pd/H-UiO-66 catalyst verified its well retained crystallite integrity and hierarchical porosity after recycling, respectively (Fig. 1 and Table 1). Besides, the metal leaching test was conducted using the residual reaction mixture of the recycling experiment after the Pd/H-UiO-66 catalyst was isolated from the ongoing reaction mixture after 1.0 h. The FFA conversion and FOL yield remained unchanged, and the Pd content of the reaction mixture was below the AAS detecting limit, confirming the heterogeneous nature of the catalyst (Fig. 7b).

In this work, the Pd/H-UiO-66 catalyst outperforms the previously reported supported metal catalysts [22,39–42] with a TOF value as high as $66.7 \, h^{-1}$ (Table S1). Based on the characterizations and reaction



Fig. 5. ATR-IR spectra of different catalysts after the adsorption of FFA.

results, we proposed the outstanding reactivity of the Pd/H-UiO-66 catalyst was related to the uniformly distributed Pd NPs and the unique hierarchically porous H-UiO-66 supports [38]. Rich mesopores throughout the H-UiO-66 bulk are believed to be beneficial to reduce the mass diffusion resistance and enhance the accessibility of Pd active sites in the FFA hydrogenation reactions. Additionally, the partially preserved micropores ensured the integrality of the H-UiO-66

crystalline and would prevent the aggregation of Pd NPs, affording good durability during the recycling.

4. Conclusions

Supported transition-metal catalysts were prepared using hierarchically porous H-UiO-66 as the supports for furfural hydrogenation to synthesize furfuryl alcohol. The uniformly distributed metal NPs on the H-UiO-66 support endow the Pd/H-UiO-66 catalysts with high Pd dispersion and thus enhanced accessibility of active sites. Consequently, a complete FFA conversion and > 99 % FOL yield were obtained over Pd/H-UiO-66 at 60 °C and 0.5 MPa H₂ in the aqueous medium within 3 h of reaction. This work may provide new perspectives for the design and fabrication of highly efficient MOF catalysts for practical applications including biomass-related conversions as demonstrated here.

CRediT authorship contribution statement

Ruiqi Fang: Conceptualization, Methodology, Software, Resources, Investigation, Funding acquisition, Writing - original draft. **Liyu Chen:** Formal analysis, Visualization. **Zirong Shen:** Formal analysis. **Yingwei Li:** Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to



Fig. 6. FOL yields as a function of time in FFA hydrogenation over Pd/H-UiO-66 with different metal loadings, reaction conditions: FFA 5.0 mmol, catalyst (metal 0.5 mol%), H_2O 5 mL, 60 °C, 0.5 MPa H_2 (a). The effect of temperatures (b), H_2 pressures (c) and solvents (d) on FFA conversions and FOL yields.



Fig. 7. Reuses of the Pd/H-UiO-66 catalyst in the furfural hydrogenation (a) and activity profile for the hydrogenation of furfural with filtrate (b). Reaction conditions: FFA 5.0 mmol, Pd/H-UiO-66 catalyst (metal 0.5 mol%), H₂O 5 mL, 60 °C, 0.5 MPa H₂.

influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.03.019.

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